

NORTH CAROLINA AGRICULTURAL AND TECHNICAL  
STATE UNIVERSITY

Department of Electrical Engineering

Greensboro, NC 27411

LANGLEY GRANT  
N-76-CR  
114844  
P. 11

Final Report

on

HETEROEPITAXIAL GROWTH OF III-V SEMICONDUCTOR COMPOUNDS

BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION FOR

DEVICE APPLICATIONS

Research Grant No. NAG-1-403

October 1983 to August 1987

Submitted to

National Aeronautics and Space Administration  
Langley Research Center  
Hampton, VA 23665

Technical Monitor: Mr. Ivan Clark

Submitted by:

Ward J. Collis, Co-Principal Investigator  
Ali Abul-Fadl, Co-Principal Investigator  
(919) 334-7762  
January 1988

(NASA-CR-182346) HETEROEPITAXIAL GROWTH OF  
3-5 SEMICONDUCTOR COMPOUNDS BY METAL-ORGANIC  
CHEMICAL VAPOR DEPOSITION FOR DEVICE  
APPLICATIONS Final Report, Oct. 1983 - Aug.  
1987 (North Carolina Agricultural and

N88-14832

Unclass

G3/76 0114844

HETEROEPITAXIAL GROWTH OF III-V SEMICONDUCTOR COMPOUNDS  
BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION FOR  
DEVICE APPLICATIONS

1. INTRODUCTION

The purpose of this research project was to design, install and operate a metal-organic chemical vapor deposition (MOCVD) system which was to be used for the epitaxial growth of III-V semiconductor binary compounds, and ternary and quaternary alloys. The long-term goal was to utilize this vapor phase deposition in conjunction with existing current controlled liquid phase epitaxy (CCLPE) facilities to perform hybrid growth sequences for fabricating integrated optoelectronic devices.

2. SYSTEM DESCRIPTION

Because of the limited facilities and personnel it was decided at the beginning of this project to purchase a basic metalorganic vapor phase epitaxy (MOVPE) system, install it in a renovated laboratory area, and modify the system as future research activities required. System specifications were established in a preliminary fashion in order to obtain estimates of cost from several vendors. A set of bid specifications was then prepared. The MOVPE system was delivered by the vendor (CVD Equipment Corp., Deer Park, NY) in June 1985. This system includes the following features: atmospheric pressure operation, two metalorganic source channels, two gas source channels, mass flow controllers, VCR fittings, a vertical 3-inch diameter reaction chamber, rotating 10 facet SiC-coated graphite susceptor, and three-ported valves for vent-run operation. A gas flow diagram for the MOVPE system is shown in Fig. 1. The cost of this system was in excess of the project funding, so other resources were utilized for the balance.

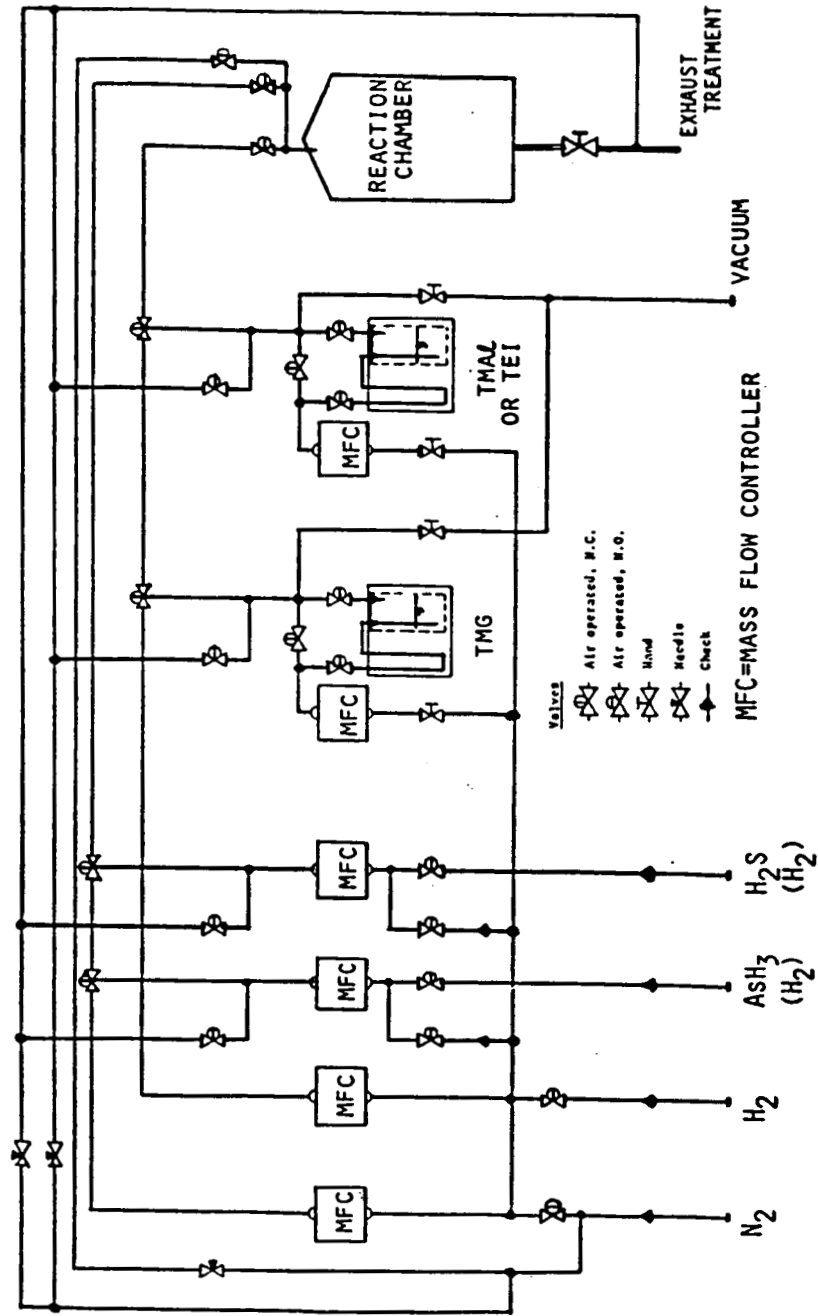


Figure 1. Schematic diagram of MOVPE gas control system.

As indicated above, the MOVPE system was quite incomplete and additional equipment and components had to be purchased with other research grant and Department of Electrical Engineering funds. These items included:

- o 7.5 kW RF generator
- o 12 SLPM hydrogen purifier
- o MDA TLD-1 single-point arsine detection system [1]
- o Portable toxic/flammable gas detector
- o Hydrogen detection system
- o Acid fume hood
- o Solvent fume hood
- o Laminar flow clean hood
- o Three laboratory exhaust systems  
(Two for the MOVPE system, one for the fume hoods)
- o Water and drain service for the fume hoods
- o Deionized water system for materials preparation
- o Components for an additional liquid source channel  
(Mass flow controller, valves, fittings, chiller)
- o Components for an additional gas source channel
- o Three cylinder gas cabinet
- o Three cross-purge gas pressure regulators
- o Self contained breathing apparatus
- o Eutectic metal purifier for arsine line.

The components of the hydrogen purifier were installed within the gas control section of the MOVPE system cabinet. In order to protect the purifier diffusion module in the event of power failure, a nitrogen purge system was designed and incorporated into the purifier installation. Many of the added components incorporated welded VCR fittings. However, the final connections to the pressure regulators involve threaded or compression fittings. A future modification may be the substitution of welded regulator/purge assemblies.

The susceptor temperature is monitored with a thermocouple in sliding contact with the quartz susceptor support tube. This is the feedback signal for the RF power controller. A single-walled quartz reactor tube is O-ring sealed to a water-cooled stainless steel baseplate. This baseplate is lowered with respect to the reactor tube with a motor drive to permit

loading/unloading of substrates.

The gas injection valves are distributed along a 1/4-inch OD manifold tube at a distance of about 24 inches from the chamber. Thus, abrupt switching of dopants or composition is not possible. Again, a future modification may be the installation of a rapid switching valve block at the entrance to the reaction chamber.

In order to provide laboratory exhaust facilities for the MOVPE system and the associated chemical fume hoods, building modifications had to be designed and approved by the University and the State. This and the contractor's delays represented quite a loss in time on the research effort. Similar delays were encountered in providing the water/drain service for the fume hoods.

Initially, GaAs will be grown in the MOVPE system. Trimethylgallium (TMG) and a 10% arsine in hydrogen mixture have been purchased for this testing of the system. The eutectic metal arsine purifier (Ga-In-Al, EMCORE Corp. [2]) will be installed after some experimental results have been obtained upon the quality of GaAs which can be grown with the existing system.

### 3. SAFETY CONSIDERATIONS

Obviously, the anticipated use of toxic substances, such as arsine and phosphine, and the development of a chemical handling laboratory has incurred many requirements by the University for safety features which must be provided by this research effort. The various features incorporated in the system and the laboratory are discussed here.

Presumably, the use of the toxic hydride gases is the most dangerous aspect of the III-V MOVPE growth process. As indicated above, two detector instruments are available for indicating the presence of these gases. The

portable unit is sensitive in the parts per million range and will be used for checking arsine cylinders at the time of delivery. It is also sensitive to hydrogen so it can be used as a system leak detector. The MDA detector unit is calibrated to alarm at 100 ppb arsine concentration (2xTLV). This unit draws a gas sample through the pick-up tube with a pump. Normally, this pick-up tube will be located in the gas cylinder cabinet. It can be moved to other locations during system testing, growth or cylinder exchange. This MDA instrument uses a chemically active paper tape as the detection medium. Hence, there is a continuing operating cost (ca. \$1,000 per year). The alarm relay of this detector has been connected to the gas cabinet exhaust fan to cause it to turn on if it happens to be off during an alarm condition.

Flow sensors are installed in the gas cabinet and reaction chamber exhaust systems to prevent or shut down system operation if the air flow is not above a set point minimum value. A pressure switch is installed in the exhaust connection to the reaction chamber. If the chamber pressure rises above ca. 3 psi, this switch will cause the inlet gas valves to shut. This is intended to prevent a dangerous pressure condition in the reactor if an exhaust line valve were closed or filters were clogged in the exhaust treatment system. The RF generator is also shut down in this situation. The hydrogen purifier has a hydrogen leak detection system to guard against a potential failure in the purifier assembly. If this detection system is activated, it will close the impure hydrogen inlet valve. Another hydrogen detector is mounted near the ceiling in the laboratory. This second unit will provide an alarm function.

The reactor exhaust and vent gases are combined and passed through a quartz tube in a 900°C pyrolytic decomposition furnace. The outlet of the

arsine gas pressure regulator cross-purge assembly is also to be connected to the cracking furnace inlet. To remove any particulate matter in the exhaust gases (e.g., arsenic), the furnace outlet is coupled to four cartridge filters in parallel. Initial operation will determine if these filters can perform for a reasonable time without clogging. The filtered gases pass through a dual chamber oil bubbler before venting into the exhaust system air flow. This exhaust system is shown schematically in Fig. 2.

Ultimately, the MOVPE system operation will create waste materials which require proper disposal. Again, the most serious waste problem is arsenic. This condenses on the reactor chamber, baseplate and the cracking furnace tube, and collects in the particulate filters and the oil bubbler. Thus, solid and liquid waste material will be accumulated. The disposal of this material will be a part of the system operating costs.

Alternative forms of exhaust treatment are available. However, the costs of these systems made their consideration impractical. A reliable method of arsine disposal involves adsorption and oxidation in a cannister of activated charcoal [2]. This cannister must eventually be replaced. Another technique is the scrubber approach employing a chemical solution to react with the exhaust gases. The waste is in the form of precipitates in a liquid. Finally, a controlled burning system can be used to convert the toxic gases into less toxic solid oxides.

Several comprehensive articles concerning the design of safe laboratory facilities for the use of metalorganics and hydrides have been published [3,4,5]. The Solar Energy Research Institute has sponsored safety conferences for the solar cell fabrication industry. These tend to concentrate upon the amorphous silicon deposition process utilizing silane

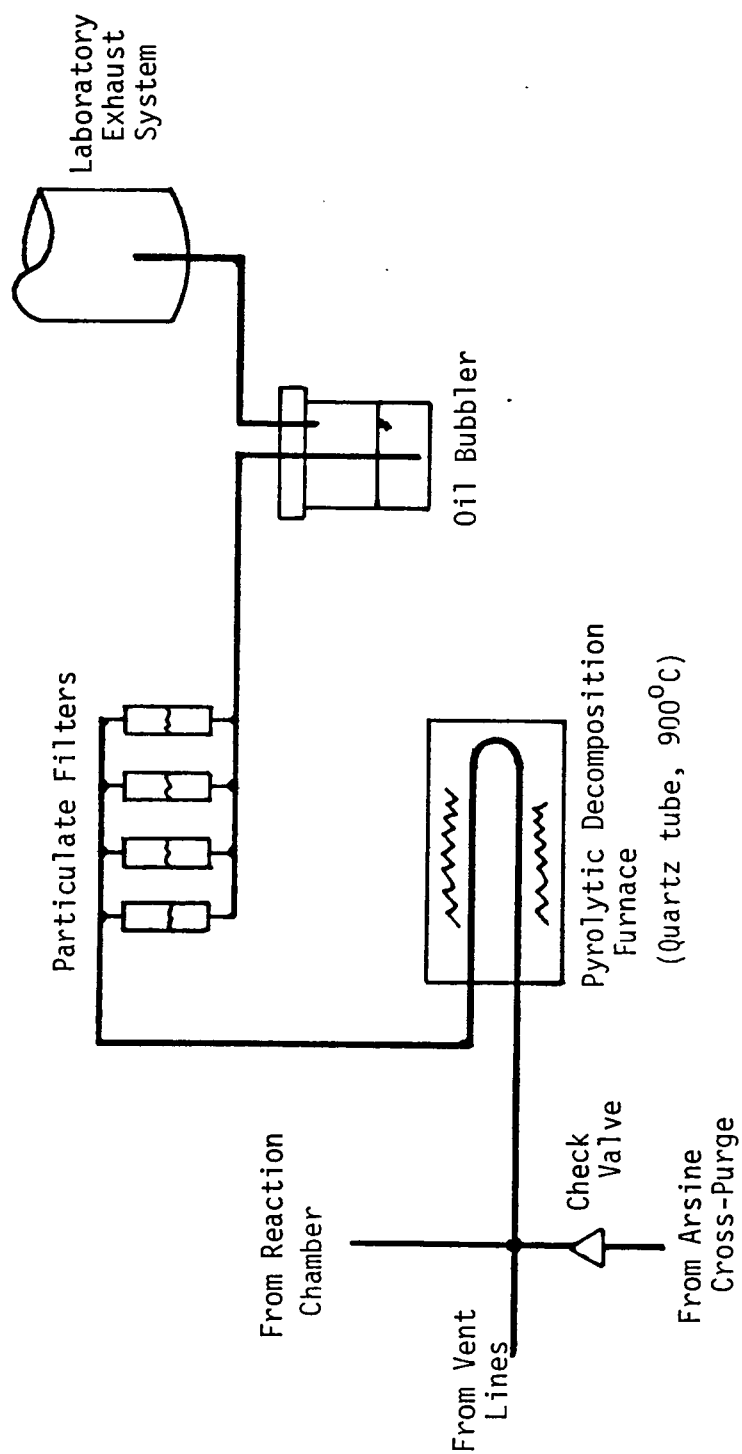


Figure 2. Schematic diagram of exhaust gas treatment system.



and refer to commercial facilities.

The highly toxic nature of arsine (and phosphine) has prompted the investigation of other compounds which might be compatible with the MOVPE process for the growth of III-V semiconductors. Organometallic arsenic sources may be potential replacements for arsine since they seem to be considerably less toxic. These materials have been recently investigated and may not have been developed yet to the purity available in commercial arsine. Trimethylarsenic [6], diethylarsine [7], and tertiarybutylarsine [8] are three liquids for which MOVPE results have been reported. The various problems associated with these substitutions include poor surface morphology, high carbon concentration and residual impurities in the epitaxial layers. There is evidence that hydrogen bonded arsenic species (e.g.,  $\text{AsH}_3$ ) reduce the incorporation of carbon as an acceptor in GaAs epitaxial layers [9]. It has been shown that substitution of helium for hydrogen as the carrier gas has negligible effect on the growth rate and carbon incorporation in arsine-based GaAs MOVPE growth [10]. Thus, there appears to be a compromise between reduced carbon acceptor incorporation in GaAs epitaxial layers using arsine and the less toxic nature of the organoarsenic compounds.

#### 4. SYSTEM STATUS

The MOVPE system at the termination of this research grant was in the final stages of the assembly of the exhaust treatment system. Welding of stainless steel components was necessary and the cracking furnace tube was being constructed by a glassblower. The MDA TLD-1 arsine detector has been recalled by the manufacturer for modification. Thus, the arsine delivery has been delayed. A remote system alarm status indicator panel is being designed so that potentially hazardous conditions might be indicated before

entering the laboratory. This is an important safety feature because the air handling system communicates with three laboratory rooms. Thus, a toxic leak situation might be distributed into the adjacent research facilities.

Two graduate students and an undergraduate student have been associated with the installation of the MOVPE system and the laboratory modifications.

The MOVPE system will be completed with other funding. Research proposals are being prepared for studying heterointerface properties and selected area, or patterned, growth techniques.

5. REFERENCES

- [1]. MDA Scientific, Inc., Lincolnshire, IL.
- [2]. For example, the Model F-301 Toxic Gas Adsorber, EMCORE Corp., South Plainfield, NJ.
- [3]. R. M. Lum, J. K. Klingert and B. V. Dutt, "An integrated laboratory-reactor MOCVD safety system," J. Cryst. Growth 75, 421 (1986).
- [4]. K. L. Hess and R. J. Riccio, "Integrated safety system for MOCVD laboratory," J. Cryst. Growth 77, 95 (1986).
- [5]. R. L. Messham and W. K. Tucker, "Design of a safe facility for the metalorganic chemical vapor deposition of high-purity GaAs and AlGaAs," J. Cryst. Growth 77, 101 (1986).
- [6]. D. W. Vook, S. Reynolds, and J. F. Gibbons, "Growth of GaAs by metalorganic chemical vapor deposition using thermally decomposed trimethylarsenic," Appl. Phys. Lett. 50, 1386 (11 May 1987).
- [7]. R. Bhat, M. A. Koza, and B. J. Skromme, "Growth of high-quality GaAs using trimethylgallium and diethylarsine," Appl. Phys. Lett. 50, 1194 (27 April 1987).
- [8]. R. M. Lum and J. K. Klingert, "Use of tertiarybutylarsine in the metalorganic chemical vapor deposition growth of GaAs," Appl. Phys. Lett. 50, 284 (2 February 1987).
- [9]. R. Bhat, "OMCVD growth of GaAs and AlGaAs using a solid As source," J. Electron. Mater. 14, 433 (July 1985).
- [10]. G. Arens, H. Heinecke, N. Pütz, H. Lüth and P. Balk, "On the role of hydrogen in the MOCVD of GaAs," J. Cryst. Growth 76, 305 (1986).